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TECHNICAL PAPER proposed for presentation at
Fifth Intersociety Energy Conversion Engineering Conference
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Abstract

Trapped electrolyte alkaline fuel cells are presently being used in aerospace applications. Low temperature versions of these systems appear to offer certain advantages over the Apollo-type fuel cell. However, the life characteristics of these low temperature cells have been somewhat disappointing. This paper presents an analysis which explains certain types of early failures of these cell systems. The effects of trace quantities of carbon dioxide in the reactant gases are investigated with particular attention paid to the progressive decrease in the electrolyte volume in cells that are operated under conditions of constant electrolyte vapor pressure. Attention is also directed to the changes in electrochemical characteristics of the electrolytes caused by the formation of potassium carbonate and to the composition of the electrolyte relative to the phase boundary between the single (liquid) phase and the two-phase (liquid plus solid) region. It is shown that poor performance of fuel cells may result from:

1. Reduction of electrolyte volume due to the formation of potassium carbonate.

2. Excessive polarization caused by the inferior electrochemical properties of heavily carbonated electrolytes.

3. Poor and erratic performance caused by precipitation of solids from the electrolyte due to operation close to the two-phase boundary line of the phase diagram.

These three factors are used to describe operational boundaries for the fuel cell. Life of the cell or stack is predicted in terms of carbon dioxide exposure and certain assumed distributions of cell to cell differences.

Introduction

Fuel cell systems for aerospace applications use hydrogen and oxygen as reactants. Some present state-of-the-art systems use an alkaline electrolyte trapped inside a matrix material. This report will describe the effect on cell performance of trace impurities which lead to the formation of potassium carbonate in the electrolyte. Further, this paper will discuss how this effect is compounded in fuel cell systems that have wide cell-to-cell variations in the optimum quantity of electrolyte. The analysis presented here will illustrate the types of information needed to select conditions that will lead to longer stack operating times. No consideration is given herein to any failure mechanism other than that caused by formation of carbonates in the fuel cell electrolyte.

It has been suggested by Szego and Cohn (Ref. 1) that based on weight considerations fuel cell systems represent the most attractive system to perform as an electrical energy supply over the time span of a few days to the greater part of a year. However, in performing endurance runs, full systems seldom run longer than a thousand hours without some form of maintenance or fix. It would be desirable for fuel cell systems to operate for 5000 to 10,000 hours before overhaul is required.

A brief description of fuel cell system water management will help in understanding the reason why certain trace impurities in the hydrogen and oxygen feed streams lead to short stack lives. In current fuel cells the water produced during operation is removed by either controlling the pressure in the water removal cavity, e.g., Allis-Chalmers (A-C) fuel cell, or by controlling the dewpoint of the recirculating hydrogen, e.g., Pratt & Whitney (P&W) fuel cell. These control devices try to prevent the cells from operating with excess water (wet) or a deficiency of water (dry). The water management control is predicated on the physical properties (vapor pressure vs. temperature) of the initial electrolyte concentration.

As potassium carbonate builds up in the electrolyte, the water vapor pressure increases. If the control device cannot differentiate the increase in vapor pressure due to carbonate build-up from other causes, and compensate accordingly, the net result will be a reduction in electrolyte volume as potassium hydroxide is converted to potassium carbonate. In cells that initially were on the dry side, the electrolyte gas-interface will move away from the more wettable electrode, resulting in failure of the cell.

Besides alterations in electrolyte volume, carbonation will produce other undesirable effects. It will lead to a decrease in the conductivity of the electrolyte and increase the possibility of precipitation of solids.

An attempt has been made in preparing this paper to gather all the pertinent physical property data of the system, water-potassium hydroxide-potassium carbonate. These properties include electrical conductivity, vapor pressure, density, and the phase diagram.

Based on this data the effect of carbonate build-up on the following was estimated: (1) electrolyte volume, interface movement and conductivity, assuming a constant vapor pressure constraint, (2) stack life, assuming hypothetical distributions of cell to cell differences, and (3) mass transport.

Performance Degradation Due to Carbonate Formation

To call attention to the deleterious effects of carbonates in alkali fuel cells, data are presented which were obtained specifically to illustrate these effects. The results of purposely adding carbon dioxide and carbon monoxide to the oxygen stream of an operating fuel cell are summarized in Table I.

This information was obtained from single cells that employed the static water removal concept (Ref. 2). In this type of arrangement reactive impurities like carbon dioxide if present in the hydrogen stream can react with either the potassium hydroxide in the water removal matrix or the potassium hydroxide in the fuel cell matrix. The information presented in Table I shows a 10-to-20 fold increase in the degradation rate of a single cell caused by the presence of 0.1 percent CO_2 or CO in the reactant oxygen. Carbon monoxide present in the oxygen stream is readily oxidized to carbon dioxide at the electrode and thus is equivalent to carbon dioxide. Degradation rates of 15 to 20 μV/hr are considered to be representative of "good" cells.

Figure 1 shows some unpublished United Aircraft polarization data taken on cells with constant electrolyte volumes for mixtures ranging from zero to 100 percent K_2CO_3 at constant potassium concentration. Several different current densities were employed in these studies. It is to be noted that these values of polarization are over and above those of pure 32 wt percent KOH solutions. This information shows that polarization increased quite markedly at high current densities and at high percentages of K_2CO_3. The 600 asf data was taken from an American Cyanimid report (Ref. 3). This same study (Ref. 3) also made some estimates of the percentage of voltage loss that was due to carbonate formation for several life tests. These estimates based on losses due to increased polarization and decreased open circuit voltages ranged from 20 to 80 percent.

Although data resulting from well controlled experiments are scarce, the material that is available all points to the conclusion that carbonate formation in the electrolyte of alkaline fuel cells must be avoided.

Physical Properties of KOH-K_2CO_3-H_2O Solutions

For purposes of analysis, a fuel cell operating temperature of 100° F has been selected. In the following discussion properties are given at this temperature, unless otherwise indicated.

1. Specific Conductance

Figure 2 shows conductivity data at 206° F from two sources (Refs. 4 and 5). To be noted are the generally higher values of conductivity from Ref. 4 which presents data for mixtures of KOH and K_2CO_3. Also plotted in this figure are lines showing the progressive carbonation of a 40 percent KOH electrolyte under the constraint of (1) constant vapor pressure, and (2) constant volume.

2. Vapor Pressure

Reference 6 presents vapor pressure data for a number of KOH-K_2CO_3-H_2O mixtures as a function of temperature. This data has been replotted (Fig. 3) in a way more suitable for the purposes of this analysis. It will be shown later that some of the mixtures selected are in a region of the phase diagram where solid $2\ KOH \cdot 3K_2CO_3$ is present. Editing of this vapor pressure data was done to take this into account.

3. Density

References 7 and 8 list density data for KOH solutions (Fig. 4). Handbook values for K_2CO_3 solutions at room temperature were reviewed. It was noted from these tabulated values that a solution that was A wt percent in KOH (at room temperature) had almost exactly the same density as a solution that was A wt percent in K_2CO_3. Further it was found that a solution that was A/2 wt percent in K_2CO_3 and A/2 wt percent in KOH had a density corresponding to A wt percent KOH. For lack of any more exact information it will be assumed in this paper that a solution that is B wt percent in KOH and C wt percent in K_2CO_3 will have a density corresponding to B plus C wt percent KOH at the temperature of interest.

4. Phase Diagram

Two references (Refs. 9 and 10) which were related to phase diagram studies were located. In general they agreed, but only the one of Luce Cabonnel (Ref. 10) is presented here (Fig. 5) since this study appeared to be more complete.

Physical Effects of Carbon Dioxide Exposure

Prior to entering into an analysis of the effects of carbon dioxide or similar gases on trapped electrolyte, alkaline fuel cells it is instructive to introduce the concept of the Unit Exposure (UE). This term and the Volume Normalized Unit Exposure (VNUE) express in a quantitative manner the amount of potassium carbonate that is formed in a cell according to the reaction:

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$$

The amount of CO_2 that enters a fuel cell is proportional to the amount of CO_2 in the reactant gases, the current density at which the cell is operating and the duration of the exposure. The Unit Exposure is defined as that amount of carbon dioxide added to a cell that is operating with an impurity level of 1 ppm CO_2 in the hydrogen stream and 1 ppm CO_2 in the oxygen stream for a 1000 hr period at a current density of 100 amperes per square foot (asf). In terms of CO_2, a Unit Exposure amounts to 2.79×10^{-3} moles of CO_2 or, in terms of KOH lost, 5.58×10^{-3} moles. The units of this parameter are moles per 10^5 ampere hours (A hr) per ft^2 of electrode area. It is assumed in this analysis that all of the carbon dioxide reacts completely with the potassium hydroxide solution in the fuel cell matrix.

Since the effect a given amount of carbonate has on the electrolyte will, to a certain extent, depend on the volume of the electrolyte, the Volume Normalized Unit Exposure was found to be a more convenient measure of carbon dioxide exposure. This term is obtained by dividing the Unit Exposure by the initial electrolyte volume per square foot of electrode area. The units of this term are moles per 10^5 A hr per ml.

As mentioned earlier, fuel cell control systems are keyed to the vapor pressure of the pure KOH-H_2O solution initially present in the fuel cell. That is, for a constant temperature of operation, a constant partial pressure of water is assumed for the electrolyte in the fuel cell. Referring back to the vapor pressure-composition relationships (Fig. 3), this means that as solutions undergo progressive carbonation, the KOH compositions will fall on a horizontal straight line on this plot. This assumption is valid if the hydrogen gas stream leaving a cell is saturated with respect to water for the carbonated electrolyte case, as is assumed for non-carbonated electrolyte.

For the purpose of illustration, four starting solutions of KOH (30, 35, 40, and 45 wt percent at 180° F) have been selected and their progressive carbonation followed using these straight, horizontal lines at constant vapor pressure. The resulting mixtures may now be placed on a phase diagram plot as shown in Fig. 6. The value of this plot can be greatly enhanced by the addition of a number of families of lines derived as follows.

1. By determining the composition as a function of the VNUE's and picking compositions at a number of constant values of the VNUE, lines of constant VNUE, UE/V_o, may be added to the plot.

2. With the help of the density data the electrolyte volume (V) can be followed as a function of carbonation and related to the starting electrolyte volume (V_o). With the help of appropriate cross plots lines of constant V/V_o may be added to the plot.

3. For convenience, carbonation may be calculated in terms of percent conversion of the original KOH. Again with the help of suitable cross plots, lines of constant percent conversion may be added to the plot.

4. Lastly, some of the phase boundary lines of the phase diagram may be added to the plot.

Figure 7 shows the addition of these lines to the previous figure and will be referred to as an isobaric carbometric chart. One further physical effect may be pointed out in this section and that is the movement of the "effective" gas electrolyte interface that results from the volume change of the electrolyte. It is assumed here that either one or both of the electrodes are able to accommodate the volume changes that take place in the electrolyte volume. Figure 8 shows the interface movement as a function of Unit Exposures for 25, 50, 75, and 100 mls of starting electrolyte volume per square foot for the case of 35 wt percent KOH at 180° F with all electrolyte shrinkage occurring in one electrode only. Movement is divided by the porosity of the electrode to obtain the interface movement in thousandths of inches. Care must be taken when using wet-proofed or flooded agglomerate pore type electrode models in applying the proper porosity value. Attention is called to the relative insensitivity of the interface movement to the volume of starting electrolyte.

Effects of Carbon Dioxide on the Mass Transport and Kinetic Aspects of Fuel Cells

Aside from the more obvious effects of carbon dioxide mentioned in the previous section, there are other more subtle but nonetheless important effects stemming from the conversion of KOH to K_2CO_3. Although these effects do not lend themselves to quantitative interpretation, for the sake of completeness they will be discussed in qualitative terms. It will be shown, that the conversion of KOH to K_2CO_3 has a detrimental effect on the cell open circuit voltage, and the kinetic, catalytic, and mass transport aspects of alkaline fuel cells.

It is helpful to first consider a cell in which the liquid volume is held constant during operation. The resulting increases in polarization with carbonation are then clearly due to the concentration changes.

A. Constant Volume Case

Modes of polarization may be associated fairly unambiguously with either the bulk liquid region or the reactive regions of the electrodes. Remarks made concerning polarization associated with the bulk liquid should hold with no qualifications in the case of a changing volume, but effects in the region of current production will in general be coupled with the changing liquid volume. Care must thus be exercised when reasoning from the constant volume case to the changing volume case.

Symbolically the separation of polarization effects is given by:

$$V_{cell} = V^o_{cell} - \eta^*_c - \eta^*_A - \Delta\Phi^*$$

Here V_{cell} is the operating voltage and V^{o}_{cell} is the open-circuit voltage of the cell under the conditions present in the cell (f(T, p, concentration, etc.)). η^{*}_{c} is the polarization associated with the cathode and measured at the bulk liquid-electrode interface, η^{*}_{A} is the polarization at the anode (as defined above), and $\Delta\Phi^{*}$ is the solution potential difference between the two interfaces at which the respective η^{*}'s are measured. The superscript * is used to emphasize position dependency.

Bulk Liquid Polarization-$\Delta\Phi^{*}$

If the conduction of current in the bulk liquid between the electrodes is considered to be one-dimensional, $\Delta\Phi^{*}$ is approximately equal to the sum of two terms - the simple ohmic voltage drop and a term proportional to the log of the ratio of the activities of the current-carrying species. In the alkaline H_2-O_2 fuel cell the current carrying species is in effect OH^{-} and the concentration gradients are such that an increase in the concentration gradient of OH^{-} ions ($\Delta C_{OH^{-}}$) across the cell yields an increase in $\Delta\Phi^{*}$.

The gradual conversion of KOH to K_2CO_3 increases $\Delta\Phi^{*}$ through contributions in both of the above terms. Experimental conductivity data (Fig. 1) shows reduction in conductivity with increasing carbonate content. It can also be shown, qualitatively at least, that $\Delta C_{OH^{-}}$ is inversely proportional to the mean concentration of OH^{-} in the liquid phase (at a given current density). Thus accumulation of $CO_3^{=}$ leads to increased ohmic drops and depletion of OH^{-} leads to increased concentration gradients.

Effects on Open Circuit Voltage - V^{o}_{cell}

The open circuit voltage is in general approximated by the reversible voltage as given by the Nernst Equation for the reaction

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$$

Variations from this reversible voltage are presumably due to the presence of a mixed potential at the cathode. The effect of OH^{-} depletion (and $CO_3^{=}$ buildup) on the HO_2^{-} equilibrium which causes the mixed potential is unknown. On the other hand, the Nernst Voltage will vary simply with carbonation. The change in reversible voltage will be proportional to the change in the log of the solution vapor pressure. It can be seen (Fig. 3) that the vapor pressure of solutions increase with percent conversion for a constant K^{+} concentration. For the case of constant volume then the reversible voltage will decrease as carbonate accumulates.

Electrode Polarization-(η^{*}_{A}, η^{*}_{c})

Elucidation of modes of electrode polarization requires knowledge of: (1) the mechanism by which the reaction takes place on the catalyst surface, (2) the distribution of active catalyst in the electrode, and (3) the rates at which reactants and products are transported to and from reaction sites.

Information in these three categories is rather sparse even where carbonation effects are not considered, and at this time no more than mention of the possible ways in which carbonate accumulation might contribute to polarization can be made.

(a) Mechanism and Kinetics

As discussed above, the cathodic potential is determined by some mechanism involving HO_2^{-}, and the effect of carbonate is unknown. If the electrode reaction does not involve peroxide the depletion of OH^{-} via carbonation might tend to favor the reaction, but the effect of OH^{-} depletion on the step(s) involving HO_2^{-} may offset this advantage.

At the anode, the depletion of OH^{-} should tend to lower the actual current density since here the OH^{-} is a reactant. This effect might be masked by the attendant enhanced solubility of gaseous H_2 in diluted KOH solutions.

(b) Active Catalyst Distribution

The distribution of catalytic material in an electrode is determined by its construction. But whether or not the catalyst in some portion of the electrode is contributing to current production depends on operating conditions. Here, in particular, the liquid volume is important.

One obvious way in which regions of the electrode may become inactive is by precipitation of solids from the electrolyte. Loss of active catalytic area by this or other process requires increased current density on the remaining catalyst surface and thereby increases electrode polarization.

(c) Transport of Reactants and Products

In general, any effect which tends to decrease the concentration of dissolved reactants at the catalyst surface reaction sites leads to increased electrode polarization. Thus, changes in reactant solubility and diffusivity in the electrolyte are reflected in polarization changes. No data exists showing carbonate influences on these properties but it is known that both quantities decrease with increasing solute concentration in hydroxide solutions. Therefore, decreases in solubility and diffusivity of the reactants may be of some importance, particularly if carbonation is accompanied by concentration of the electrolyte (decrease in volume).

Potential gradients in the electrodes arise because current production is distributed through the electrode. These potential gradients are very similar in nature to those in the bulk electrolyte. The situation within the electrodes is much more complex than within the bulk electrolyte and in order to calculate this form of polarization the spatial distribution of current production as well as the physical properties of the electrode must be known. However, as in the bulk electrolyte, the potential gradients in the electrodes should increase with carbonate accumulation. This increase in potential gradient has the effect of increasing the electrode polarization at all points in the electrode including the plane at which η^{*}_{A} or η^{*}_{c} is measured. Thus, carbonate formation may alter considerably the transport characteristics of both dissolved gaseous reactants and liquid species.

B. Changing Volume Case

The more realistic case is one where there is a continual decrease in electrolyte volume as carbonation proceeds. The two areas that have been previously discussed that are most sensitive to changes in electrolyte volume are discussed below.

1. Catalyst Usage

Of foremost importance is the effect of liquid volume on what might be called the efficiency of catalyst use. Clearly the most efficient cell operation is that in which a maximum amount of catalyst surface is engaged in current production.

To remain active a given catalyst site must be: (1) immersed in the electrolyte, (2) in close proximity to a gas-liquid interface area, and (3) connected via a continuous, relatively short liquid path to an active site on the other electrode. All three of these requirements depend on the volume of liquid in the cell. The exact dependency is difficult to assess, being related to the microscopic character of the electrode in question, but a catalyst site initially active may become inactive as the liquid volume decreases through eventual violation of one or more of the three requirements. As mentioned before any loss of active area results in an increase in the current density elsewhere, which in turn increases electrode polarization.

2. The Concentrating Effect

Volume decreases are also manifested in a "concentrating" effect on the electrolyte since volume losses are normally losses of H_2O as vapor, and it appears that this has an adverse effect on mass transfer of all species in the liquid phase (charged and uncharged). This decrease in conductivity might be minimized if the initial concentration of KOH was on the dilute side of the conductivity maximum instead of at the maximum as is usually the case.

Fuel Cell Failure Mechanisms

It is appropriate at this point to discuss certain types of failure mechanisms in fuel cell systems. Failures caused by malfunctioning

pumps, valves, electronic equipment, etc. will not be discussed in this paper. Only failures resulting from gradual decreases in stack voltage will be considered. Although low cell voltage is the usual criteria of cell or stack failure, there are three separate conditions that could be the cause of these low voltages.

1. Cell operation with the electrolyte in a region of the phase diagram where two phases are present

2. Excessive polarization losses due to the inferior electrochemical properties of heavily carbonated electrolytes

3. Loss of electrolyte interface between one of the electrodes and the matrix due to volume losses in the cell caused by carbonation effects

It will now be shown that each of these three aspects of poor performance will lead to an operation boundary on the isobaric carbometric chart (Fig. 7).

If systems are meant to be started and stopped with rest periods at or about room temperature, then the 75^{o} F phase boundary represents one of these operational boundaries. Based on the discussions of the previous section relating to the concentration differences occurring due to the mass transport processes, it is premature to suppose that limiting operation to the 75^{o} F phase boundary line will alleviate precipitation of solids at all current densities while operating at 180^{o} F. However, as a minimum, operation should be terminated at this boundary condition.

The next operational boundary will be that dictated by polarization limitations. Figure 1 shows the polarization that would be experienced as a function of percent conversion of the KOH. Although this data is somewhat sketchy, especially at the higher current densities, it does represent the type of information required for the particular cell configuration of interest. By knowing the current density at which the cell must operate and still maintain a particular voltage level, as dictated by the power conditioning equipment, a degree of carbonation can be selected which would represent the cut off as far as polarization is concerned. One hundred millivolts of polarization over and above that due to pure KOH solution appears to be tolerable. As an example, for 200 asf operation, 60 percent conversion of the KOH to carbonate (35 percent KOH) could probably be tolerated. This adds a second possible limiting boundary to the main figure (for this current density, the 60 percent conversion line).

The third and final limiting condition concerns permissible volume losses. This requires data not only of what might be called "volume tolerance" of a cell, but the distribution of cell-to-cell differences between the upper and lower critical volumes, as well as the optimum volume of the cells that go into making a stack.

The concept of volume tolerance can be introduced with the help of Fig. 9. A cell that has a deficiency of electrolyte performs poorly due to a progressive loss of interface between the matrix and the electrode. This condition can also lead to gas crossover, burn-through, and non-recoverable losses of catalytic activity. The lower critical volume (V_L) is defined as that volume below which continued cell or stack operation would result in the aforementioned difficulties. At the opposite end of the spectrum, a cell that contains too much electrolyte will either weep or lose its electrochemical active area. The upper critical volume (V_U) is defined as that volume above which poor performance and/or loss of electrolyte results. The curve of cell voltage as a function of volume is bound at both sides and most likely exhibits a maximum at what is defined as the optimum volume (V_{op}). In addition to volume losses due to carbonation, cell weepage and electrolyte creepage result in additional volume losses. As stated before, this paper will consider only volume losses due to the effects of CO_2.

Distribution of Cell-to-Cell Differences

Information on distributions of cell-to-cell differences is not generally available except for some limited proprietary data. Therefore, for purposes of this paper, hypothetical distributions will be generated. In practice, to determine V_{op}, a single cell is placed in a test stand after being loaded with a known volume of electrolyte solution of known concentration. The cell is started and operated at a constant current density and some relationship assumed for the electrolyte volume as a function of either the humidity of the exiting hydrogen gas or pressure of the water removal cavity. The cell is then subjected to "wetting" and "drying" conditions and a cell voltage versus the calculated electrolyte volume is determined. This "volume optimization curve" as it will be called shows a maximum at the optimum volume. And, dependent on the range of conditions imposed, the volume optimization curve may also reveal the values of the upper and lower critical volumes. Among any group of cells there will be a distribution of values for each of the parameters V_{op}, V_L, and V_U.

This results from the cumulative effects (distributions) of such things as:

1. Experimental errors in the volume optimization process and errors in vapor pressure data

2. Manufacturing tolerances on electrode and matrix porosity, thickness, density, etc.

3. Non-measureable causes such as improper catalyst distribution, effects of pore size distribution on electrolyte holdup, etc.

The central limit theorem of statistics states that the distribution of a parameter resulting from the cumulative affects of a number of independent variables will tend towards being normal. It was found, however, to be convenient to use a Poisson distribution in this particular instance in that the generated distribution was easier to fit with the boundary conditions. The boundary conditions are as follows. Let the distribution as to the lower critical volume be considered. It is expected that the mean V_L would be close to the electrode matrix interface, since by definition the lower critical volume is that volume below which the electrode is in danger of losing proper interface between the electrode and matrix. The distribution must be bounded on the less-than-mean-side by the physical limitations of cells not operating at all when the gas-electrolyte interface recedes into the matrix material. On the greater-than-the-mean side of the distribution there are no physical bounds. Thus, a tail resulting from the degree of quality control placed on the manufacturing operation will exist. The same argument may be applied to the "expected" distribution of the upper critical volume.

The assumptions and ground rules for generating these synthetic distributions will now be listed.

1. It will be assumed that one of the electrodes is more wettable than the other and this more wettable one will define the volumes as illustrated in Fig. 10.

2. Two different values of the parameter m, the mean of the Poisson distribution, will be selected for the sake of comparing stack lives resulting from a "good" and a "bad" cell-to-cell distribution.

3. Two different values of V_m/V_M will be selected for the sake of comparing cells with thick matrices to those with thin matrices.

4. The distributions will contain a total of 36 cells.

5. The distributions of V_U and V_L shall touch in the case of the bad distribution.

6. The volume span of the more wettable electrode shall be 20 units.

These distributions are shown in Fig. 11. Here the two Poisson distributions having mean critical volumes of 2 and 3 volume units are drawn. It is supposed that even perfect cells cannot operate at V_m and V_M. Therefore, cell class 0 is offset from both limits. The offset from V_M is greater in recognition of the need for a supermeniscus film in wetting electrodes.

The importance of these types of distributions becomes more evident when a stack is assembled and filled with electrolyte in the usual manner. There are two general methods for filling a stack in preparation of running a full system. One is called dry stacking. In this method the stack is assembled and then electrolyte is admitted to the

assembled device. In this method a dilute solution of KOH is used and in general each cell absorbs the same quantity of electrolyte. In the wet-stacking method, electrolyte is applied to each cell prior to assembly. Although both these methods have deficiencies, the dry stacking method appears to be favored. The shortcoming of both methods is that each cell is filled with an amount of electrolyte that only on the average (at best) is the correct amount. Some cells will have more than the optimum volume and some will have less than the optimum volume. In anticipation of volume losses during stack operation an attempt is made to start with all cells slightly on the wet side. The shape of the cell-to-cell distribution does not always allow this however. But unless the wettest cell contains more than the upper critical volume ($V \geq V_U$) and/or the driest cell contains less than the lower critical volume ($V \leq V_L$) the stack may be safely operated.

Stack Life as Affected by Cell-to-Cell Distributions and Carbon Dioxide Exposures

An attempt is made to start a stack with the average cell somewhat on the wet side of the optimum. It should be obvious that some discretion must be exercised since the stack should not even be started if any cell has a V/V_U greater than 1.0 (an overly wet cell). Indeed with a wide distribution of cell-to-cell differences some cells must be removed from the stack and replaced with cells closer to the average before it can be started. Once a stack is started, operation must cease as soon as the driest cell falls below a V/V_L value of 1.0

Figure 12 shows the amount of electrolyte in each of the 36 cells (by cell class) after a filling procedure that resulted in the average cell being filled with 1.15 times the average of V_U and V_L. Also plotted are the volume distributions resulting from several values of carbon dioxide exposure measured in Volume Normalized Exposure Units. This plot was generated for an operating temperature of 180° F, a 30 percent KOH starting solution, the Poisson distribution characterized by $\bar{m}$ equal to 3, and V_m/V_M equal to 0.25. It can be seen from this figure that under this filling procedure cell, class 8 would prevent the stack from starting. Attention should be called to the fact that in the real situation the lines in Fig. 12 would be bands resulting from the volume swings which in turn result from power swings during stack operation. The wider the power swings to be expected during stack operation and the poorer the controls system on the fuel cell stack, the wider the bands will be.

In Table II are tabulated values for the ratio of the lower critical volume to the starting volumes as a function of quality control ($\bar{m}$ in Poisson distribution), cell selection (rejection of certain cell classes), and V_m/V_M. This information is interpreted as follows. If the value of $V_o/V_U \leq 1$ the stack will be operable. The value of V_L/V_o is a measure of the volume loss that can be tolerated in the driest cell before the value of V_L/V equals 1.0 (termination of operation). In essence these values are measures of the tolerable values of V/V_o.

This now completes the third operational boundary which may be placed on the main figure. To be noted are the significant increases in tolerance to volume decreases which result from either a tighter cell-to-cell distribution or simply a cell selection procedure that culls out the cells that will tend to run on the dry side when placed in a stack. Also noteworthy is the fact that cells with thin matrices ($V_m/V_M = 0.25$) are more tolerant to volume decreases than cells with thick matrices ($V_m/V_M = 0.5$). However, cells with thicker matrices (more electrolyte/ft^2) undergo less volume loss per unit of CO_2 exposure.

Therefore, there will be associated with each type of distribution an allowable volume decrease during the course of operation. If the distribution is known for the cells that go into making a stack, the allowable volume decrease is calculable in terms of the ratio of the volume at cutoff to starting volume. The significance of the lines of constant V/V_o now become evident.

All three of these operational boundaries are somewhat sensitive to the current density at which the stack is meant to operate. This is caused by the fact that at high current densities higher polarization losses, larger concentration gradients and larger volume swings resulting from the power swings are present. These factors tend to shrink the area on the main plot that represent permissible operation. The net effect of a smaller area for permissible operation is a shorter stack life based on CO_2 tolerance.

Given the three operational boundaries based on the conditions selected for operating the stack, a selection of the initial KOH concentration may still be made to maximize stack life. For a given initial KOH concentration, the carbonation line is followed until the first operational boundary is met. For different initial KOH concentrations, this will usually result in different values of UE/V_o at the cutoff. The object of this exercise is to maximize the value of UE/V_o where the first operational boundary is met.

By way of examples a single cell will be examined first. The operational boundaries will be assumed to be the following based on a maximum current density of 200 asf.

1. V/V_o - 0.80
2. Percent conversion - 60 (100 mV of added polarization)
3. Phase boundary line - 75° F

For a starting solution of 30 wt percent KOH the V/V_o boundary line would terminate operation at $UE/V_o \cong 0.7$. For a starting solution of 37.5 wt percent KOH the percent conversion boundary line would terminate operation at $UE/V_o \cong 0.95$. If a starting solution of 45 wt percent KOH had been selected, the phase boundary line would terminate operation at $UE/V_o \cong 0.6$.

In terms of operating times, these volume normalized unit exposures must be converted to regular unit exposures by multiplying by the volume of original electrolyte per square foot of electrode. As an example, assuming 50 ml/ft^2 of electrolyte, an impurity level of 3 ppm CO_2 in the gas streams, and 100 asf as the average current density, for the maximum value of $UE/V_o = (0.95)$, the corresponding time of operation would be:

$$t = \frac{0.95 \times 50}{(3/1)(100/100)} \times 1000 = 15,800 \cong 16,000 \text{ hr}$$

For a UE/V_o of 0.6 the corresponding time of operation would be 10,000 hr. These times are almost unheard of for fuel cell systems or even full 28 volt stacks, but have been achieved in some recorded single cell tests.

The difficulty associated with predicting the life of a 30-cell stack lies in knowing the cell-to-cell distribution of the group of cells going into it. Based on the generated cell-to-cell distribution where the permissible volume loss was 6 percent ($V_L/V_o = 0.94$), and assuming this would be halved by the requirement to withstand volume changes due to power swings, an estimate of stack life can be made. The V/V_o limit will now be 0.97. This would decrease the value of UE/V_o to about 0.2 (35 wt percent KOH). Using the other assumptions of the single cell example, the value for time of operation would be 3300 hr. It is significant that system and full-stack tests rarely exceed this value. More specific conclusions cannot be made due to the absence of long-term data from tests which were sufficiently monitored and controlled with respect to reactant impurity level.

It is desirable that a cell stack be able to start up without preheating to the operating temperature (180° F in the above example). The volume change of the electrolyte due to temperature effects must now be taken into account. From room temperature to 180° F there is an electrolyte expansion of between 3 and 4 percent. The operating time of the above mentioned stack is now reduced from 3300 to 0 hr by this consideration. This point exemplifies the large effect on stack life that can result from rather small electrolyte volume changes.

As the operational boundaries are shifted to correspond to different stack characteristics (operational current density, tolerable V/V_o, etc.) the electrolyte concentration which yields the largest value of UE/V_o also changes.

It should be remembered that although this analysis is not based on any assumptions, it did entail the use of some questionalbe and sketchy data on the physical properties of these three component mixtures. In order to apply the analysis in a meaningful way to real

fuel cell systems the following information is required.

1. More accurate physical properties data
2. Accurate distributions of cell-to-cell differences in regard to the volumes that are of interest
3. Accurate relationships between the average electrolyte concentration at different power levels

Conclusions

An analysis is presented which investigates the effects of carbon dioxide impurities in the reactant gases of hydrogen-oxygen fuel cells. This analysis is limited to the case where electrolytes are maintained at a constant vapor pressure. Based primarily on changes in the physical properties of alkaline electrolytes (conductivity, volume, and vapor pressure) operational boundaries are estimated. Operation outside of these boundaries would lead to poor or zero cell performance.

The life of a cell or stack is predictable (based on the effects of carbon dioxide) if certain basic information is known about the cell, the distribution of certain cell-to-cell differences, and the characteristics of the control system on a fuel cell system. The life of a fuel cell system was shown to be very sensitive to the following:

1. The level of CO_2 in the reactant gases
2. The performance - electrolyte volume relationship of the cell
3. The distribution of certain cell-to-cell differences
4. The initial concentration of the electrolyte
5. The volume of the electrolyte used in filling a stack of fuel cells
6. The characteristics of the control system used on the fuel cell system

Before this analysis can be applied quantitatively to present day fuel cell systems, more accurate data are required on some of the physical properties of these three component solutions.

References

1. Szego, G. C. and Cohn, E. M., "Fuel Cells for Aerospace Application," Astronautics and Aerospace Engineering, Vol. 1, No. 4, May 1963, pp. 107-111.
2. Anon., "Research and Development on Fuel Cell Systems," NASA CR-80607, Oct. 1966, Allis-Chalmers Mfg. Co., Milwaukee, Wisc.
3. Gershberg, D., Colman, W. P., Olson, K. E., and Schmitz, E. W., "High-Performance Light-Weight Electrodes for Hydrogen-Oxygen Fuel Cells," CR-1216, 1968, NASA, Washington, D.C.
4. Usanovich, M. I. and Sushkevich, T. I., "Electric Conductivity and Viscosity in the System $KOH-K_2CO_3-H_2O$," Journal of Applied Chemistry of the USSR, Vol. 24, 1951, pp. 657-659.
5. Klochko, M. A. and Godneva, M. M., "Electric Conductivity and Viscosity of Aqueous Solutions of Sodium and Potassium Hydroxides," Zhurnal Neorganicheskoi Khimii, Vol. 4, 1959, pp. 2127-2135.
6. Anon., "Research and Development on Fuel Cell Technology," NASA CR-84971, Feb. 1967, Allis-Chalmers Mfg. Co., Milwaukee, Wisc.
7. Anon., Solvay Technical Bulletin, No. 15, table 5.
8. Walker, R. D., Jr., "A Study of Gas Solubilities and Transport Properties in Fuel Cell Electrolytes," SAR-6, NASA CR-106407, Feb. 1969, University of Florida, Gainesville, Fla.
9. Kamino, Y. and Miyaji, M., "Manufacturing of Alkali Carbonates. I. Solid-Liquid Equilibrium of Na_2CO_3-NaOH-H_2O and K_2CO_3-KOH-H_2O Systems," Denki Kagaku, Vol. 34, No. 11, 1966, pp. 914-917.
10. Carbonnel, L., "Contribution to a Study of a Binary System Water-Carbonate and Potassium and a Ternary System Water-Carbonate and Potassium-Potash," Revue de Chimie Minerale, Vol. 1, 1964, pp. 115-124.

TABLE I

	Test 1		Test 2	
	Ultrapure H_2 and O_2	Ultrapure H_2 0.1 percent CO_2 in O_2	Ultrapure H_2 and O_2	Ultrapure H_2 0.1 percent CO in O_2
Current density, ma/cm^2	107.7	107.7	107.7	107.7
Elapsed time, hr	0 → 352	352 → 622	0 → 450	450 → 710
Time averaged degradation rate, $\mu V/hr$	73.6	1031.7	~45	~700

TABLE II. - EFFECTS ON PERMISSIBLE VOLUME DECREASE OF QUALITY CONTROL, CELL SELECTION AND MATRIX THICKNESS

Tabulated values of V_L/V_o

	Thin matrices, $V_m/V_M = 1/4$	Thick matrices, $V_m/V_M = 1/2$
Wide distribution ($\bar{m} = 3$) (all cell classes)	>1.0 ($V_U/V_o > 1$)	>1.0 ($V_U/V_o > 1$)
Wide distribution ($\bar{m} = 3$) (Reject cell class 8 - 1.2 percent of cells)	0.88	0.94
Wide distribution ($\bar{m} = 3$) (Reject classes 7 and 8 - 3.4 percent of cells)	.78	.87
Wide distribution ($\bar{m} = 3$) (Reject classes 6, 7, and 8 - 8.4 percent of cells)	.69	.82
Narrow distribution ($\bar{m} = 2$) (all cell classes)	.78	.87
Narrow distribution ($\bar{m} = 2$) (Reject class 6 - 1.7 percent of cells)	.69	.82

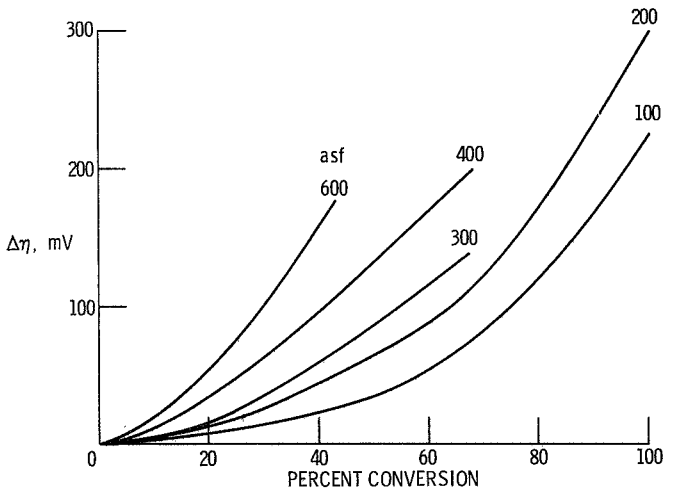


Figure 1. - Polarization against percent conversion at constant electrolyte volume, P&W unpublished data.

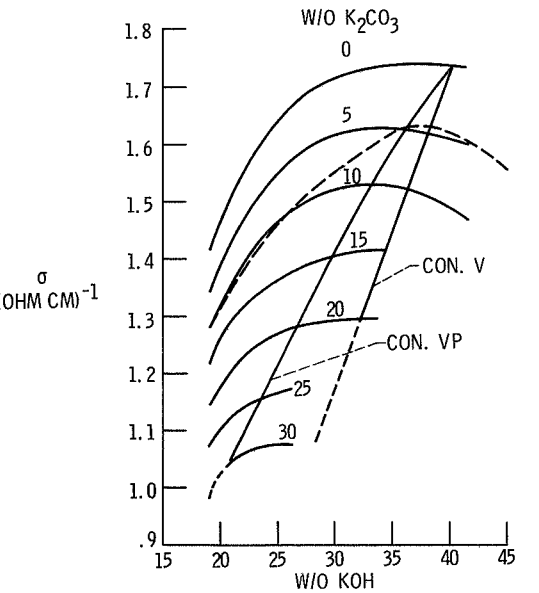


Figure 2. - Conductivity versus concentration at 206° F.

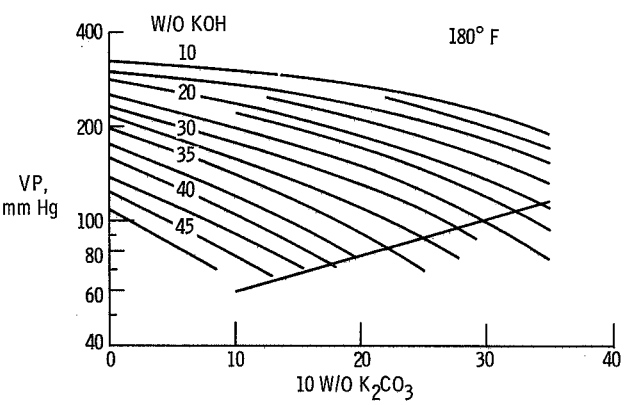


Figure 3. - Vapor pressure of mixtures of H_2O, KOH, and K_2CO_3.

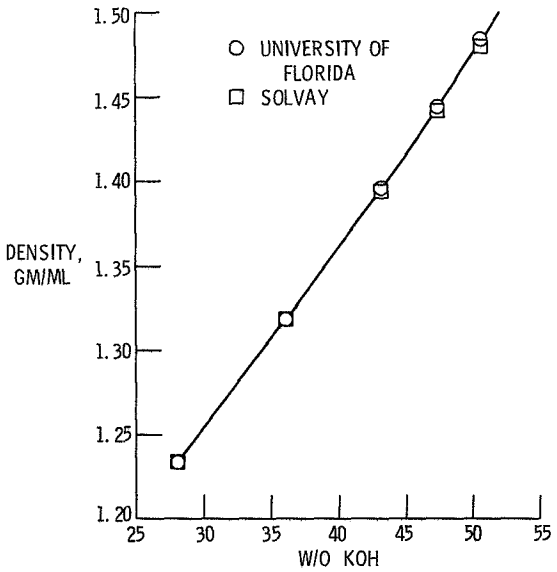


Figure 4. - Concentration versus density of solutions of H_2O and KOH at 176° F.

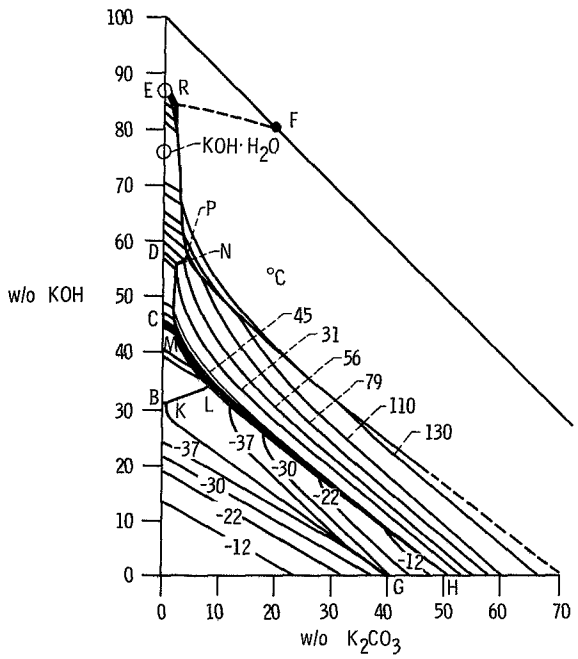


Figure 5. - Phase diagram of the system H_2O-KOH-K_2CO_3.

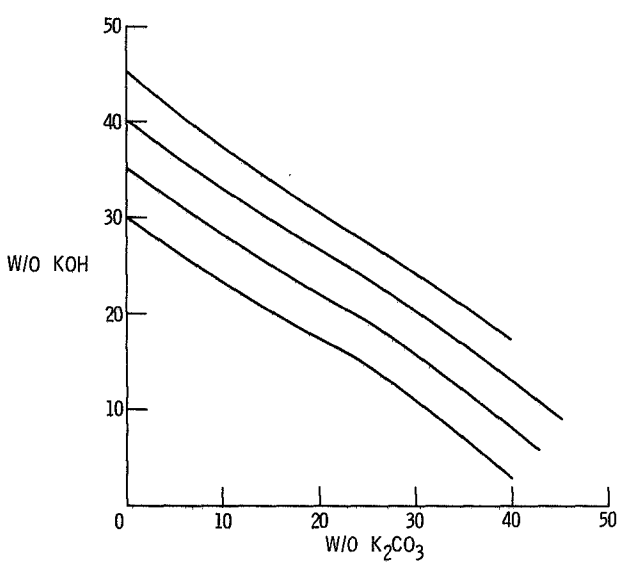


Figure 6. - Isobaric carbonation lines of several KOH solutions at 180° F.

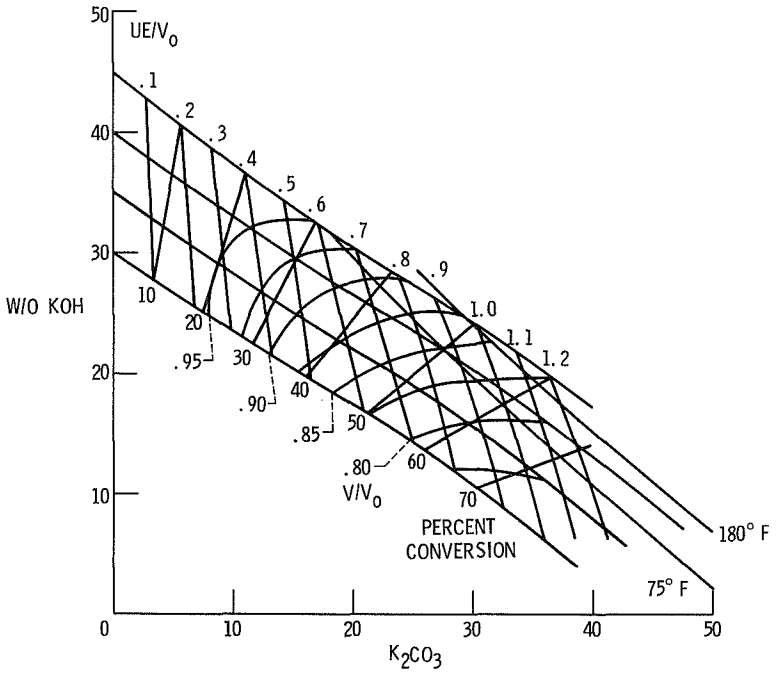


Figure 7. - Isobaric carbometric chart at 180° F.

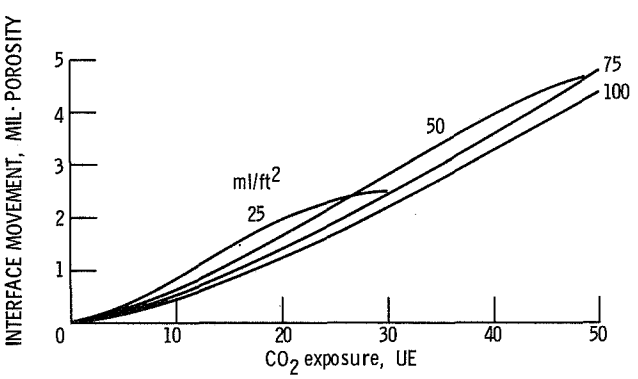


Figure 8. - Interface movements as a function of CO_2 exposure for cells of different electrolyte loadings.

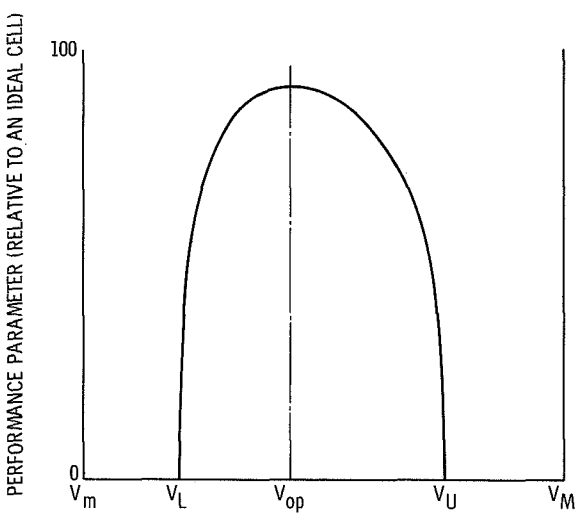


Figure 9. - Cell performance versus volume of contained electrolyte.

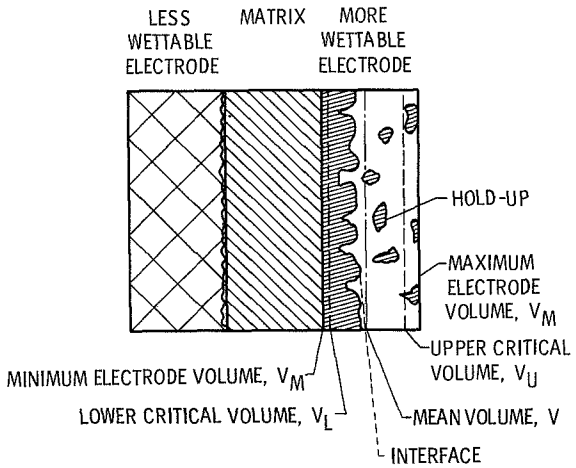


Figure 10. - Definition of pertinent electrode volumes.

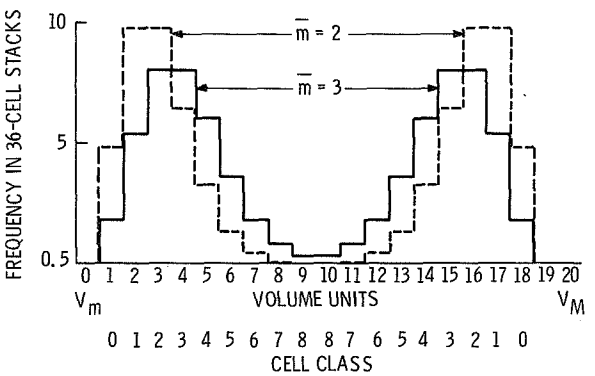
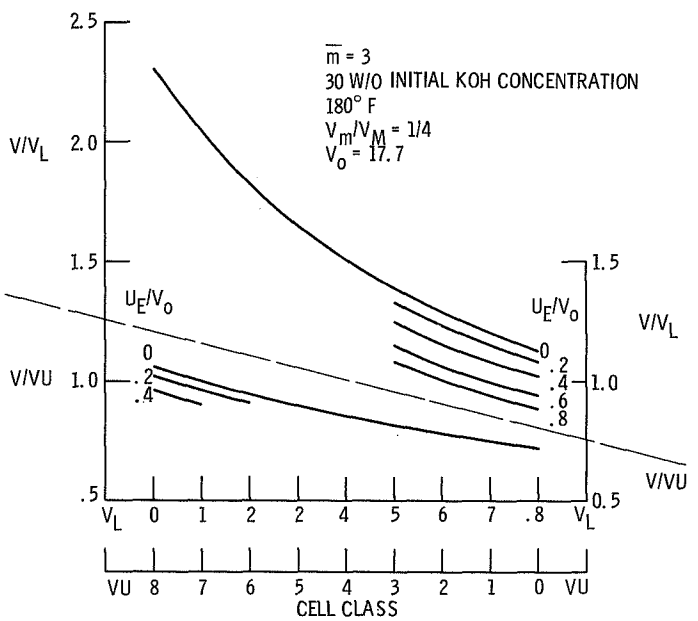


Figure 11. - Cells classified according to Poisson distribution of critical volumes.



V_L: WITH RESPECT TO LOWER CRITICAL VOLUME
VU: WITH RESPECT TO UPPER CRITICAL VOLUME

Figure 12. - Ratios of cell volume to critical volume for various values of unit exposure according to cell class.

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